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**(54) Title:** COMPOSITION AND METHOD FOR INHIBITING THE CURE OF CYANOACRYLATE ADHESIVES AND CURE INHIBITED CYANOACRYLATE ADHESIVE COMPOSITIONS

**(57) Abstract**

Compositions and methods for inhibiting the cure of cyanoacrylate adhesives and cure inhibited cyanoacrylate adhesive compositions. The cure inhibited compositions comprise an organic carboxylic acid; and a hydrated or anhydrous metal chloride, fluoride, bromide or iodide.

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-1-

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10                   COMPOSITION AND METHOD FOR INHIBITING THE  
                  CURE OF CYANOACRYLATE ADHESIVES AND CURE-  
INHIBITED CYANOACRYLATE ADHESIVE COMPOSITIONS

Background of the Invention

Field of the Invention

15                  This invention relates to compositions containing cyanoacrylate adhesives that are temporarily inhibited from polymerizing and curing even in the presence of activating substances, such as metals, which normally catalyse polymerization of cyanocrylate adhesive compositions. This invention also relates to compositions and methods for inhibiting polymerization and curing of cyanoacrylate  
20                  adhesives.

Description of the Prior Art

25                  A major drawback of cyanoacrylate compounds is their tendency to polymerize rapidly and often uncontrollably when contacted or mixed with various activating substances, especially substances that form ions in solution. Even trace quantities of such activators as organic salts, inorganic salts, metals, water, urea, oxides, etc., substantially increase the rate of cyanoacrylate polymerization. This tendency has limited the usefulness of cyanoacrylate compounds to ordinary adhesive applications. If cyanoacrylate compounds could be mixed with sufficient quantities of various activating substances without polymerizing immediately, they would be useful in a wide variety of additional applications.  
30

35                  The development of cyanoacrylates, such as methyl-2-cyanoacrylate, ethyl-2-cyanoacrylate, propyl-2-cyanoacrylate, 2-ethylhexyl-2-cyanoacrylate, isobutyl-2-

-2-

1 cyanoacrylate, n-butyl-cyanoacrylate, hexyl-, heptyl-, and  
octyl-cyanoacrylate, etc., represented a major technological  
advance in the bonding and adhesive art.

The preparation of cyanoacrylates is well-known.  
5 It is described in such U.S. Patents as No. 2,467,926; No.  
2,794,788; No. 2,912,454; and No. 2,926,188, the disclosures  
of which are incorporated by reference. The use of cyano-  
acrylate polymers as adhesives is described in such U.S.  
Patents as No. 2,776,232; No. 2,794,788; and No. 2,467,926,  
10 also incorporated by reference. The cyanoacrylate adhesives  
are fast-drying, high tensile-strength glues and bonding  
agents. Their use in bonding or joining materials together  
is very widespread in industry, in the household, and in  
special applications such as surgery (as tissue adhesives),  
15 dentistry, etc.

Various inorganic substances have been proposed  
as fillers or thickeners for cyanoacrylate monomer composi-  
tions. For example, U.S. Patent No. 3,663,501 of Adams, et  
al. issued on May 16, 1972 discloses preparation of a  
20 dental cement containing finely divided sodium fluoride,  
fused silca, quartz, and alumina fillers. U.S. Patent No.  
3,607,542 of Leonard, et al. issued on September 21, 1971  
discloses the preparation of water-resistant cyanoacrylate  
paste containing insoluble inert fillers (such as various  
25 salts of calcium, titanium, zinc, tin, aluminum and iron)  
for use as adhesives in submerged applications and as  
fillings for teeth. Neither reference is concerned with  
the polymerization rate of cyanoacrylate adhesives or with  
its control.

Incorporation of acid inhibitors in cyanoacrylate  
30 compositions is known. For example, U.S. Patent NO.  
4,182,823 of Schoenberg issued on January 8, 1980 teaches  
that acid additives called "stabilizers" in the patent)  
including acid gases, other acids (such as acetic) or  
various Lewis acids (such as  $\text{FeCl}_3$ ,  $\text{SnCl}_2$  and  $\text{BF}_3$ ) inhibit  
35 polymerization of cyanoacrylate compositions. The patent  
warns, however, that such additives must be used with

-3-

1 caution because strong acids "over-stabilize" the monomer  
and weak acids do not "stabilize" it sufficiently. Schoen-  
berg further observes that the acids (which are said to act  
as anionic polymerization inhibitors) interfere with the  
5 cure of the adhesive.

U.S. Patent No. 2,794,788 of Coover issued on  
June 4, 1957 states that sulfur dioxide is effective as a  
stabilizer for cyanoacrylate monomers, that boron trifluo-  
ride and hydrogen fluoride are also effective, but that  
10 carbon dioxide is less effective.

U.S. Patent No. 4,460,759 of Robins issued July  
17, 1984 discloses a two-part cyanocrylate adhesive compo-  
sition. One part of this composition contains weakly  
acidic or weakly ionic compounds as accelerators for  
15 polymerization, particularly when these compositions are  
used on wood substrates. Such accelerators are said to  
include metal halides. The first part contains acid gases  
and free-radical compounds as inhibitors.

Although many of the above references recognize  
20 the need to control the rate of polymerization of cyano-  
acrylate adhesives, the additives they propose are inade-  
quate as inhibitors because their inhibitory effect cannot  
be well-controlled.

As stated in Schoenberg, supra, too little  
25 acid inhibitor is not effective and too much can interfere  
with polymer cure. In addition, many acid additives cause  
polymer decomposition, and shorten the useful life of the  
cyanoacrylate polymer.

Accordingly, it is an object of the present  
30 invention to provide novel compositions useful as inhibitor-  
stabilizers for cyanoacrylate compounds and compositions.

Another object is to provide novel inhibiting-  
stabilizing compositions for cyanoacrylates that effectively  
35 delay onset and propagation of polymerization reactions  
even in the presence of activators for such reactions.

Another object is to provide cyanoacrylate compo-  
sitions that are temporarily or permanently rendered non-  
reactive to activating substances.

## SUBSTITUTE SHEET

-4-

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Another object of the invention is to provide cyanoacrylate compositions that are temporarily or permanently inhibited from polymerizing in which the inhibitor does not cause premature decomposition of the polymer.

5

Another object is to provide cyanoacrylate compositions that are temporarily or permanently inhibited from polymerizing to a controlled extent although they contain substantial amounts of substances that act as catalysts for cyanoacrylate polymerization.

10

Another object is to provide cyanoacrylate compositions that are electrically or thermally conductive and have such polymerization and stability characteristics or mechanical properties as make them suitable for use in the manufacture of electronic and microelectronic components.

15

Another object is to expand the uses to which cyanoacrylate adhesive compositionis can be put by providing compositions comprising cyanoacrylate monomers that are controllably inhibited towards polymerization and at the same time yield polymers with the desired degree of cure and stability.

20

A further object is to prepare cyanoacrylate adhesive compositions that can be spray-coated in place using inter alia on artists' air brush.

25

Yet another object is to provide methods for inhibiting the polymerization of cyanoacrylate compounds and for preparing polymerization-inhibited and stabilized compositions containing cyanoacrylate compounds and activators.

#### Summary of the Invention

30

One aspect of this invention is directed to a composition comprising at least one organic acid and at least one hydrated or anhydrous base metal fluoride, chloride, bromide or iodide. The composition is useful in inhibiting-stabilizing cyanoacrylates.

35

Another aspect of the invention is directed to a cyanoacrylate composition temporarily or permanently inhibited from polymerizing, the composition including an

-5-

1      organic acid and at least one hydrated or anhydrous metal fluoride, chloride, bromide or iodide. The composition may include a filler that is ordinarily an activator of cyanoacrylate polymerization.

5           Yet another aspect of the invention relates to a method for inhibiting cyanoacrylates against polymerization by incorporating either to said cyanoacrylates or to an activator additive thereof an inhibitor comprising a liquid organic acid and an anhydrous or hydrated metal fluoride, chloride, bromide or iodide, prior to mixing said cyanoacrylate with said activator-additive, or simultaneously therewith.

DETAILED DESCRIPTION OF THE INVENTION

15     In accordance with the present invention, unpolymerized (or partially polymerized) cyanoacrylate compositions can be temporarily (or permanently) inhibited from reacting with polymerization-activating materials (activators) and at the same time stabilized against incomplete cure and/or premature decomposition.

20     This inhibition-stabilization of the cyanoacrylate is accomplished by incorporating an inhibitor-stabilizer either in the unpolymerized (or partially polymerized) cyanoacrylate or in an activator that will serve as an additive or filler of the final composition, said inhibitor-stabilizer comprising:

- (a) an organic carboxylic acid; and
- (b) a hydrated or anhydrous metal chloride, fluoride, bromide or iodide.

25     The inhibitor-stabilizer is preferably incorporated in the cyanoacrylate adhesive (monomer or prepolymer) prior to exposure of the latter to an activator, such as a metal, oxide, ionic solvent, salt, water or urea. However, it can also be incorporated to the activator prior to mixing it with the cyanoacrylate. The ingredients of the inhibitor-stabilizer must be premixed and may not be separately incorporated in the cyanoacrylate or activator.

-6-

1 Preferably, the inhibitor-stabilizer also includes a polar solvent to facilitate mixing with and  
5 solubility in the cyanoacrylate (or activator additive). In fact, unless the two active ingredients of the inhibitor-  
10 stabilizer are fully compatible with the cyanoacrylate (or activator-additive), use of a solvent is particularly desirable. Additional solvent may be used when the inhibitor-stabilizer is mixed with the cyanoacrylate to facilitate mixing. This additional solvent may but need  
not be a polar solvent; it can be any suitable organic solvent.

15 Suitable solvents for the inhibitor include polar organic and inorganic solvents, such as water, lower aliphatic alcohols, lower aliphatic ketones, lower aliphatic ethers of carboxylic acids, lower alkylene glycols, lower alkylene glycol ethers, lower aliphatic esters of carboxylic acids, carboxylic acid nitriles, and mixtures thereof.  
20 Methyl chloride, formaldehyde and dimethyl sulfoxide are also useful as solvents in the present invention.

25 Preferred solvents are: water; acetone, methyl ethyl ketone, methyl propyl ketone, methyl isobutyl ketone, ethyl butyl ketone, acetyl acetone; methanol, ethanol, propanol, isopropanol, butanol, isobutanol, and hexanol, ethyl acetate, propyl acetate, isopropyl acetate, butyl acetate, and methyl-CELLOSOLVE<sup>R</sup>-acetate (methyl-2-ethoxy-  
30 ethanol acetate; CELLOSOLVE<sup>R</sup> is a trademark of Union Carbide Corporation); ethyl ether, dimethyl ether, and diethylene glycol ethyl ether (diethyl-CARBITOL<sup>R</sup>; a trademark of Union Carbide Corporation); methyl-CELLOSOLVE, butyl CELLOSOLVE, methyl glycol ether, butoxy triglycol, methoxy triglycol, glycol methyl CARBITOL; and acetonitrile.

35 The most preferred solvents for use in the present invention are: water, acetone, ethanol, ethyl acetate, dimethyl ether, glycol methyl CARBITOL, and acetonitrile.

Preferred acids for the inhibitor-stabilizer are formic acid, acetic acid, propionic acid, butanoic

-7-

1 acid, lactic acid, pentenoic acid, carbonic acid, etc.  
Most preferred is formic acid.

Preferred metal halide salts are:  $\text{FeCl}_3$ ;  
5  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ;  $\text{LiF}$ ;  $\text{CdCl}_2$ ;  $\text{CdCl}_2 \cdot 2-1/2\text{H}_2\text{O}$ ;  $\text{MgBr} \cdot 6\text{H}_2\text{O}$ ;  
 $\text{SnBr}_4$ ;  $\text{GeCl}_4$ ;  $\text{MgCl}_2$ ;  $\text{ZnCl}_2$ ;  $\text{ZnBr}$ ;  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ;  
 $\text{LiI} \cdot 3\text{H}_2\text{O}$ ;  $\text{LiI} \cdot \text{H}_2\text{O}$ ;  $\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$ ; and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ . Magnesium  
bromide hexahydrate, tin chloride hexahydrate and ferric  
chloride hexahydrate are most preferred.

10 Non-polar solvents that can be added to the inhibited cyanoacrylate composition include without limitation plasticizers, such as dibutyl phthalate, tricresyl phosphate, dimethyl phthalate, etc.

15 Generally suitable relative proportions of the ingredients of the inhibitor-stabilizer, i.e. the acid, salt and solvent (if any) are: acid -- about 0.002 - 55%; salt -- about 0.002 - 50%; and solvent -- about 0 - 75% by weight.

20 As a weight percentage of the cyanoacrylate monomer the inhibitor-stabilizer can be about 0.10-55%.

25 The above proportions are given by way of guidelines. The actual amount of the inhibiting-stabilizing composition will depend on how long it is desired to delay the onset of polymerization for the final cyanoacrylate mixture (i.e. after addition of the activating substance) and, to a lesser extent, on the ability of the activator to catalyze cyanoacrylate polymerization. It should be noted that as the percentage compositive of acid and salt is increased, the cure time of the adhesive composition increases.

30 The duration of the stabilization or inhibition provided by a given stabilizer/acrylate formulatin is also dependent upon the ambient temperature to which the material is exposed. Storage of an inhibited cyanoc rylate compound of the present invention at 120°F for 3 weeks would result in some curing of the adhesive, however, if the same composition were stored at 40°F for 3 months little or no curing would take place.

-8-

1 By varying the ratio of inhibitor ingredients to  
cyanoacrylate constituents in the present invention, it is  
possible to inhibit curing for periods varying between a  
few minutes and  
5 several months.

10 The incorporation of the inhibitor-stabilizer  
renders the cyanoacrylate non-reactive to activating  
substances for a period of time at least long enough to  
permit mixing of the cyanocrylate with the activator and  
any processing, storage, or fabrication necessary for the  
particular end application envisioned.

15 By the present invention, a multitude of applica-  
tions become possible. The following are listed for  
illustration purposes only.

15 1) Electrically Conductive Cyanoacrylate  
Compositions and Materials

20 Incorporation of a metal with high conductivity  
(in powder or other particulate form) as a filler can  
render a cyanoacrylate composition electrically conductive.  
Before the present invention, it was impossible to incorpo-  
25 rate sufficient metal as a filler to render the polymer  
electrically conductive because rapid polymerization of the  
cyanoacrylate would begin immediately following addition  
of even minute quantities of metal. This made further  
addition of metal impossible. Moreover, rapid polymeriza-  
tion of the metal-filled cyanoacrylate would interfere with  
the processing or fabrication of the finished product.

30 Metal-filled cyanoacrylate polymers can be  
used in die and wire bonding of microelectronic circuits  
instead of solder. In addition, they can be used as  
conducting terminals for resistors, as electrodes for  
capacitors and for a variety of functions in thick-film  
hybrid microelectronic circuits. The metal-filled cyano-  
35 acrylate compositions can be applied to circuit boards by  
conventional screening methods. Electrically conductive  
cyanoacrylate compositions preferably contain about 0.5 -

-9-

1      7.0% of inhibitor, 0.05 - 0.4% acid, 0.08 to 0.8% salt and  
about 0.4% to 10.0% solvent by weight of the cyanoacrylate  
monomer.

5      Other applications for conductive cyanoacrylates  
are in high-conductivity metallization films and coatings  
for plastics, paper, mica, ceramics and other non-conductive  
materials. The metallized films and coatings allow direct  
soft-soldering without the use of flux and may be further  
10     metal-coated by electroplating. Such films and coatings  
are useful in electronic and microwave applications as  
connectors, contacts, magnetic shields, especially in metal  
shields that are used to protect from Radio Frequency  
Interference (RFI) and Electro Magnetic Interference (EMI)  
15     and capacitor terminals. They can be applied by brushing,  
dipping, or spraying, or by conventional screening tech-  
niques using standard 180 to 200 mesh screens.

20     These conductive, film-forming cyanoacrylate  
compositions preferably contain about 1.0 - 7.0% inhibitor-  
stabilizer (0.07 to 0.6 acid, 0.2 to 1.3% salt) and about  
1.0 - 10.0% solvent.

25     Suitable metal fillers for electrically conduc-  
tive cyanoacrylates, in general, include one or more of  
palladium, silver, copper, tin, gold, and platinum and  
other high-conductivity metals. The metal filler may first  
be combined with the inhibitor composition and the metal-  
containing inhibitor may subsequently be introduced into  
the cyanocrylate. This makes it possible to package these  
constituents separately for mixing by the consumer just  
prior to use (as an A&B component system).

30     2) Thermally Conductive Cyanoacrylate  
Compositions and Materials

35     Incorporation of fillers can also produce thermo-  
conductive materials that can be used as heat sinks for  
the base and mounting stud of transistors, diodes, and  
rectifiers; and as coupling agents to reduce thermal  
contact resistance. Suitable fillers for this purpose  
include base metals, such as iron, aluminum, tin, and metal  
oxides that are not electrically conductive, etc.

-10-

1        Another use for thermally conductive cyanoacrylates is for application between, e.g., semiconductor power devices and heat sinks; power resistors and chassis mounts; thermostats and mounting surfaces; and anywhere else where  
5        the efficient transfer and removal of heat are necessary or desirable. Finally, they can be used in thermoelectric devices (e.g. in transformers as anti-static layers and heat sinks) and in heat dissipaters for electronic devices.  
10      Suitable fillers for this purpose are base metal oxides (especially alumina) and iron, graphite, titanium, tin; gold, silver, copper and all heavy metals.

15      Thermally conductive cyanoacrylate compositions according to this invention preferably contain about 1.0 to 7.0% inhibitor 0.07 to 0.6% acid, 0.2 to 1.3% salt and about 1-11% solvent.

20      The thermally conductive cyanocrylates of the present invention can be used in place of other thermoconductive plastic materials including thermoconductive epoxies containing alumina or other metals. These thermal cyanoacrylates may be employed to join heat sinks and other components to printed circuit boards and in like applications.

3) Photoconductive Cyanoacrylate Compositions and Materials

25      In general, these are liquid or screenable paste (slurry) compositions that can be used in the manufacture of photocells used for light sensors, light-controlled relay operations, exposure meters, fire detectors, photometers, lamp controls, liquid level indicators and a variety of other detectors. Suitable fillers include cadmium sulfide, cadmium selenide and cadmium-sulfoselenide. Compositions used in these applications preferably contain about 0.5 - 0.2% acid about 0.08 - 0.24% salt and about 1 - 11% solvent.

35      It will be understood by those skilled in the art of the present invention that a variety of other fillers

-11-

1 can be incorporated to the inhibited-stabilized cyanoacrylates contemplated herein. These include one or more of plasticizers, silicones, silica, polymeric fillers, fibers, magnetic resins, pharmaceuticals, dyes, water, non-polar  
5 solvents, radioactive materials, viscosity modifiers, human and animal skin, etc.

10 This invention is for use with any cyanoacrylate monomer (or prepolymer) including but not limited to those set forth in the Background of the Invention, or mixtures thereof.

15 The invention will be further described below by reference to specific examples, which are intended to illustrate it without limiting its scope. Thus, the scope of the present invention is not to be limited to the cyanoacrylates, fillers, acids, salts and solvents or proportions disclosed in the Examples, below.

EXAMPLE 1

A stabilizing-inhibiting composition with or without a solvent is formed by mixing the following ingredients:

20	<u>Formula (A)</u> 40.7% $\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$ 40.7% Water 18.6% Formic Acid	<u>Formula (B)</u> 15.9% $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$ 15.9% Water 7.3% Formic acid 30.5% Acetone 30.5% Ethyl Cellosolve
25		

30	<u>Formula (C)</u> 23.5% $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ 23.5 Acetone 53.0% Formic Acid	<u>Formula (D)</u> 50.0% $\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$ — 50.0% Acetic Acid
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35	<u>Formula (E)</u> 15.9% $\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$ 30.5% Butoxyethylene glycol 15.9% $\text{H}_2\text{O}$ 7.3% Formic acid 30.5% Acetone	
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-12-

**1    EXAMPLE 2**

An inhibited-stabilized methyl-2-cyanoacrylate composition is made by mixing one of the stabilizing-inhibiting compositions according to Example 1 with methyl-  
 5    2-cyanoacrylate monomer and a solvent to improve mixing. The resulting compositions in weight percent are shown in the table below:

	Inhibited Cyanoacrylate	I	II	III	IV
	<u>Composition No.</u>				
10	Inhibitor (Any one of Ex. 1)	0.05	0.5	18.0	0.8
	Acetone	2.0	2.0	3.0	0.8
	Methyl Cyanoacrylate	97.95	97.5	76.0	98.2
	Methyl-CELOSOLVE <sup>R</sup>	—	—	—	0.2
	Ethyl Acetone	—	—	3.0	—

**15    EXAMPLE 3**

An electrically conductive cyanoacrylate composition is formed from the inhibited-stabilized compositions No. II of Example 2 and the following ingredients:

	Inhibited-Stabilized C.A.	84.0 (II)	50.0 (II)	35.0 (II)	
.20	Gold Powder	16.0	—	—	
	Silver Powder	—	37.0	—	
	Tin Powder	—	—	65.0	
	Copper Powder	—	13.0	—	
		—	—	—	
25		100.00	100.00	100.00	

These compositions will not polymerize for about 24 hours from incorporation of the metal powders.

**EXAMPLE 4**

A thermoconductive cyanoacrylate composition is formed from the inhibited-stabilized cyanoacrylate compositions No. III of Example 2 and the following ingredients:

	Inhibited-Stabilized C.A.	50.0 (III)	49.0 (III)	54.0 (III)	
	Copper Powder	50.0	—	—	
	Iron Powder	—	40.0	—	
	Thulium Powder	—	—	36.0	
	Tungsten Powder	—	21.00	10.0	

The thermoconductive compositions will not polymerize for about 24 hours from incorporation of the metal powders.

-13-

1      EXAMPLE 5

A fiber-filled cyanoacrylate composition is prepared as outlined above, except that the cyanoacrylate compositions No. IV and II were used.

5	Inhibited-Stabilized C.A.	85.0 (IV)	92.0 (II)
	Paper Fiber	5.0	—
	Wool Fiber	10.0	8.0

These compositions will not polymerize for about 24 hours after incorporation of the fibers. They can be used as adhesives, especially in high impact resistant applications and in joining sheet and cloth materials (e.g. textile fabrics, leather and vinyl sheets).

10      EXAMPLE 6

A flexible plasticized cyanoacrylate composition for use as a caulking material is prepared by mixing the inhibitor-stabilized cyanoacrylate of Example 2 with the following ingredients:

	Inhibited-Stabilized C.A.	99.2 (IV)	90.0 (II)
	Plasticizer		
20	[Propylene carbonate]	0.8	5.0
	Plasticized polyvinyl acetate	—	5.0

EXAMPEL 7

A sprayable cyanoacrylate composition containing finely divided silver particles was prepared by admixing a stabilized-inhibited cyanoacrylate composition (Formula I of Example 2 prepared with inhibitor Formula E of Example 1) with 30 percent by weight of the stabilized inhibited cyanocrylate composition of finely divided metallic silver particles (average size 200-300 mesh). The silver powder is stirred in with a single blade electric laboratory mixer until an essentially homogeneous silver dispersion is obtained. The silver containing cyanoacrylate mixture is loaded into the reservoir of a Badger brand artists' air brush. The brush is connected to a source of pressurized air (30-40 psi). Plastic sheets (each approximately 2" x 2" x 1/4") of Styrene, ABS and acrylic (plexiglass) were laid on a flat surface.

-14-

1        A solution of 5% toluidine was coated on the  
upper surface of the ABS plastic sheet and allowed to dry  
at room temperature (15°C).

5        The silver-containing cyanoacrylate composition  
was sprayed across the entire upper surface of the three  
plastic sheets (with the nozzle of the air brush held  
approximately eight inches from the surface of each sheet)  
using broad sweeping strokes.

10      At the conclusion of the spraying operation, a  
second sheet of styrene was applied to the cyanocrylate  
sprayed surface of the first styrene sheet and pressed down  
momentarily (using band pressure).

The cyanocrylate on the ABS sheet cured in  
approximately 3 minutes.

15      The cyanocrylate joining the styrene sheets  
cured to working condition (i.e. to a condition in which  
the sheets could not be pulled apart by hand) in approxi-  
mately fifteen minutes.

20      The cyanoacrylate on the acrylic sheet cured  
within one hour.

25      The method for making the compositions of the  
present invention employed in the specific embodiments  
described above is basically the same regardless of the  
particular cyanoacrylate, activator-filler and inhibitor-  
stabilizer used.

As those skilled in the art will appreciate, many  
modifications, additions, omissions and substitutions can  
be made, all within the scope and spirit of the present  
invention as claimed below.

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-15-

What is claimed is:

1. A composition useful in inhibiting polymerization of cyanoacrylate in the presence comprising from about 0.002 to about 55% of an organic acid or mixture of organic acids and from about 0.002 to about 50% of a salt selected from the group consisting of hydrated and anhydrous base metal chlorides, fluorides, bromides and iodides and mixtures thereof, said percentages being by weight.

2. The composition of claim 1 also comprising from 0 to about 75% of a polar solvent.

3. The composition of claim 2, said solvent being selected from the group consisting of water, aliphatic alcohols, lower alkylene glycols, lower alkylene glycol ethers, carboxylic acid nitriles and mixtures thereof.

4. The composition of claim 1, said acid being selected from the group consisting of formic acid, acetic acid, propionic acid, lactic acid, pentenoic acid, butyric acid, carbonic acid, and mixtures thereof.

5. The composition of claim 1, said salt being selected from the group consisting of:  $\text{FeCl}_3$ ;  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ; LiF;  $\text{CdCl}_2$ ;  $\text{CdCl}_2 \cdot 2-1/2 \text{H}_2\text{O}$ ;  $\text{MgBr} \cdot 6\text{H}_2\text{O}$ ;  $\text{SnBr}_4$ ;  $\text{GeCl}_4$ ;  $\text{MgCl}_2$ ;  $\text{ZnCl}_2$ ; ZnBr;  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ;  $\text{LiI} \cdot 3\text{H}_2\text{O}$ ;  $\text{LiI} \cdot \text{H}_2\text{O}$ ;  $\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$ ;  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ; and mixtures thereof.

6. The composition of claim 3 said acid being selected from the group consisting of formic acid, acetic acid, propionic acid, lactic acid, pentenoic acid, butyric acid, carbonic acid and mixtures thereof.

7. The composition of claim 6, said salt being selected from the group consisting of:  $\text{FeCl}_3$ ;  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ; LiF;  $\text{CdCl}_2$ ;  $\text{CdCl}_2 \cdot 2-1/2 \text{H}_2\text{O}$ ;  $\text{MgBr} \cdot 6\text{H}_2\text{O}$ ;  $\text{SnBr}_4$ ;  $\text{GeCl}_4$ ;  $\text{MgCl}_2$ ;  $\text{ZnCl}_2$ ; ZnBr;  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ;  $\text{LiI} \cdot 3\text{H}_2\text{O}$ ;  $\text{LiI} \cdot \text{H}_2\text{O}$ ;  $\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$ ; and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and mixtures thereof.

-16-

8. The composition of claim 4, said salt being selected from the group consisting of:  $\text{FeCl}_3$ ;  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ;  $\text{LiF}$ ;  $\text{CdCl}_2$ ;  $\text{CdCl}_2 \cdot 2-1/2 \text{H}_2\text{O}$ ;  $\text{MgBr} \cdot 6\text{H}_2\text{O}$ ;  $\text{SnBr}_4$ ;  $\text{GeCl}_4$ ;  $\text{MgCl}_2$ ;  $\text{ZnCl}_2$ ;  $\text{ZnBr}$ ;  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ;  $\text{LiI} \cdot 3\text{H}_2\text{O}$ ;  $\text{LiI} \cdot \text{H}_2\text{O}$ ;  $\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$ ; and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and mixtures thereof.

9. The composition of claim 1, said acid being formic acid.

10. The composition of claim 1, said salt being selected from the group consisting of  $\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$ ;  $\text{MgBr} \cdot 6\text{H}_2\text{O}$ ;  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ; and mixtures thereof.

11. The composition of claim 3, said acid being formic acid.

12. The composition of claim 3, said salt being selected from the group consisting of  $\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$ ;  $\text{MgBr} \cdot 6\text{H}_2\text{O}$ ;  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ; and mixtures thereof.

13. The composition of claim 11, said salt being selected from the group consisting of  $\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$ ;  $\text{MgBr} \cdot 6\text{H}_2\text{O}$ ;  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ; and mixtures thereof.

14. The composition of claim 9, said salt being selected from the group consisting of  $\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$ ;  $\text{MgBr} \cdot 6\text{H}_2\text{O}$ ;  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ; and mixtures thereof.

15. The composition of claim 14, said solvent being selected from the group consisting of water, acetone, acetonitrile, ethanol, ethylene glycol, ethyl acetate, dimethyl ether, and glycol methyl carbitol.

16. The composition of claim 15 comprising about 1 - 55% of said acid and about 1 - 45% of said salt.

17. The composition of claim 16 comprising about 5 - 40% of said acid, about 5 - .40% of said salt and about 1 - 60% of said solvent.

-17-

18. An adhesive composition comprising:

- (a) a monomeric ester of cyanoacrylic acid; and
- (b) an inhibitor comprising:

(i) an organic acid and (ii) a metal halide salt; said composition being inhibited from polymerizing when mixed with polymerization-activating substances.

(ii) a metal salt selected from the group consisting of  $\text{FeCl}_3$ ;  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ;  $\text{LiF}$ ;  $\text{CdCl}_2$ ;  $\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ ;  $\text{MgBr} \cdot 6\text{H}_2\text{O}$ ;  $\text{SnBr}_4$ ;  $\text{GeCl}_4$ ;  $\text{MgCl}_2$ ;  $\text{ZnCl}_2$ ;  $\text{ZnBr}$ ;  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ;  $\text{LiI} \cdot 3\text{H}_2\text{O}$ ;  $\text{LiI} \cdot \text{H}_2\text{O}$ ;  $\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$ ;  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ; and mixtures thereof;

said composition being inhibited from polymerizing when mixed with polymerization-activating substances.

19. The composition of claim 18 wherein said acid is selected from the group consisting of formic acid, acetic acid, propionic acid, lactic acid, pentenoic acid, butyric acid, carbonic acid, and mixtures thereof.

20. The composition of claim 19, wherein said solvent is selected from the group consisting of water, acetone, acetonitrile, ethanol, ethylene glycol, ethyl acetate, dimethyl ether, and glycol methyl carbitol.

21. The composition of claim 20, wherein said inhibitor is present in an amount between about 0.1% and about 50% by weight based on said cyanoacrylic acid monomer.

22. The composition of claim 21, wherein said inhibitor is present in an amount between about 1 and about 20% by weight based on said cyanoacrylic acid monomer.

23. A composition according to claim 22 further comprising a solvent selected from the group consisting of water, acetone, acetonitrile, ethanol, ethylene glycol, ethyl acetate, dimethyl ether, and glycol methyl carbitol.

-18-

24. A composition according to claim 23 wherein said inhibitor is present in an amount between about 1 and about 25% and said solvent is present in an amount between 0 and about 60% based on said monomer.

25. A composition according to claim 24, said composition further comprising a substance selected from the group consisting of activators that would catalyze polymerization of said monomer but for the presence of said inhibitor.

26. A composition according to claim 25, said composition being an electrically conductive composition.

27. A composition according to claim 26, said composition being a thermally conductive composition.

28. A composition according to claim 27, said composition being a photoconductive composition.

29. A method for stabilizing a cyanoacrylate adhesive composition so that said composition is inhibited from polymerizing when mixed with substances activating said polymerization, said method comprising:

adding to said composition in an amount effective to inhibit said polymerizatin an inhibitor comprising:

(a) an organic said selected from the group consisting of formic acid, acetic acid, propionic acid, lactic acid, pentenoic acid, butyric acid, carbonic acid, and mixtures thereof;

(b) a salt selected from the group consisting of  $\text{FeCl}_3$ ;  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ;  $\text{LiF}$ ;  $\text{CdCl}_2$ ;  $\text{CdCl}_2 \cdot 2-1/2 \text{H}_2\text{O}$ ;  $\text{MgBr} \cdot 6\text{H}_2\text{O}$ ;  $\text{SnBr}_4$ ;  $\text{GeCl}_4$ ;  $\text{MgCl}_2$ ;  $\text{ZnCl}_2$ ;  $\text{ZnBr}$ ;  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ;  $\text{LiI} \cdot 3\text{H}_2\text{O}$ ;  $\text{LiI} \cdot \text{H}_2\text{O}$ ;  $\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$ ;  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ; and mixtures thereof;

prior to or simultaneously with addition of an activating substance.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/US86/01047

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) <sup>3</sup>	
According to International Patent Classification (IPC) or to both National Classification and IPC INT. CL. 4 C08F 20/42, 4/06; C08J 3/14, 3/16; C08L 37/00, 39/00; H01C 13/00 US CL. 252/380, 501.1, 512; 256/188.31; 156/331.2; 524/548; 526/100, 298	C09K 3/00; H01B 1/02
II. FIELDS SEARCHED	
Minimum Documentation Searched <sup>4</sup>	

Classification System	Classification Symbols
U.S.	526/100, 298; 156/331.2; 252/188.31, 380, 501.1, 512; 524/548

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>5</sup>	

III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>14</sup>		
Category <sup>6</sup>	Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>
X	US,A, 4,182,823, Published 08 JANUARY 1980, SCHOENBERG. See the entire document.	1-29
X	UK,A, 2,078,763, Published 13 JANUARY 1982, KOSUKE LIDA. See the entire document.	1-29
Y	US,A, 4,125,494, Published 14 NOVEMBER 1978, SCHOENBERG. See the entire document.	1-29
Y	US,A, 3,968,186, Published 06 JULY 1976, TOMASCHEK ET AL. See the entire document.	1-29
Y	US,A, 4,460,759, Published 17 JULY 1984, ROBINS. See the entire document.	1-29
Y	US,A, 3,254,111, Published 31 MAY 1966, HAWKINS ET AL. See the entire document.	1-29
Y	US,A, 3,527,841, Published 08 SEPTEMBER 1970, WICKER, JR. ET AL. See the entire document.	1-29
Y	US,A, 3,720,656, Published 13 MARCH 1973 MANAKA. See the entire document.	1-29

\* Special categories of cited documents: <sup>19</sup>

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION	
Date of the Actual Completion of the International Search <sup>2</sup>	Date of Mailing of this International Search Report <sup>2</sup>
29 JULY 1986	18 AUG 1986
International Searching Authority <sup>1</sup>	Signature of Authorized Officer <sup>20</sup> <i>N. Sarofim</i> N. SAROFIM
ISA/US	

Form PCT/ISA/210 (second sheet) (May 1986)

**III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)**

Category *	Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No <sup>18</sup>
A	US,A, 4,377,490, Published 22 MARCH 1983, SHIRASHI ET AL. See the entire document.	1-29
A	US,A, 4,196,271, Published 01 APRIL 1980, YAMADA ET AL. See the entire document.	1-29
A	US,A, 4,102,945, Published 25 JULY 1978, GLEAVE. See the entire document.	1-29
A	US,A, 4,170,585, Published 09 OCTOBER 1979, MOTEGI ET AL. See the entire document.	1-29
A	US,A, 2,765,332, Published 02 OCTOBER 1956, COOVER, JR. ET AL. See the entire document.	1-29
A,P	US,A, 4,556,700, Published 03 DECEMBER 1985, HARRIS ET AL. See the entire document.	1-29
A	US,A, 3,354,128, Published 21 NOVEMBER 1967, WICKER. See the entire document.	1-29
A	US,A, 3,435,012, Published 25 MARCH 1965, NORDLANDER. See the entire document.	1-29